

NASA CASE NO. LAR 15266-1-CUPRINT FIG. 1*P-14***NOTICE**

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(NASA-Case-LAR-15266-1-CU) SURFACE  
ACOUSTIC WAVE OXYGEN PRESSURE  
SENSOR Patent Application (NASA-  
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## AWARDS ABSTRACT

### SURFACE ACOUSTIC WAVE OXYGEN PRESSURE SENSOR

NASA Case No.: LAR 15266-1-CU

Surface acoustic wave (SAW) pressure measuring devices of the prior art are based on the change in resonant frequency caused by the mechanical force of pressure on the piezoelectric material of the SAW device. If the piezoelectric material is fabricated as a thin membrane and arranged in such a way that the force of pressure causes the membrane to distort or flex, the sensitivity of the device can be enhanced somewhat. However, SAW pressure sensors of this type lack sensitivity for the measurement of pressures below 100 Pa.

By the present invention, a transducer is provided which is useful in measuring absolute gas-state oxygen pressure from low pressures (pressures less than 100 Pa) to atmospheric pressure ( $1.01 \times 10^5$  Pa). This was accomplished by providing a SAW device having a piezoelectric material which is coated with a chemical that will selectively and reversibly bind oxygen.

The novelty of the invention resides in the coating which is used on the piezoelectric material of the SAW device. This coating is a chemical which will selectively and reversibly bind oxygen. When oxygen is bound by the coating on the SAW device, the mass of the coating increases by an amount equal to the mass of the bound oxygen. An increase in the mass of the coating caused by the bound oxygen causes a corresponding decrease in the resonant frequency of the SAW device.

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Initial Evaluator: George Wood

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## SURFACE ACOUSTIC WAVE OXYGEN PRESSURE SENSOR

Origin of the Invention

5           The invention described herein was jointly made by employees of  
the United States Government and a NASA Contractor employee in the  
performance of work under NASA Contract NAS1-19858 with Old  
Dominion University and is subject to the provisions of Public Law 96-517  
(35 U.S.C. 202) in which the contractor has elected not to retain title.

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Background of the Invention1. Field of the Invention

15           This invention relates generally to oxygen pressure sensors. It  
relates particularly to an oxygen pressure sensor prepared by coating a  
surface acoustic wave (SAW) piezoelectric device with an oxygen binding  
agent tailored to provide variable sensitivity.

2. Description of the Related Art

20           The theory and applications of surface elastic waves have been  
reviewed. R. M. White, "Surface Elastic Waves", Proceedings of the  
IEEE, Vol. 58, No. 8, August 1970, pp. 1238-1276. Since publication of  
25 a work by Wohltjen and Dessy (H. Wohltjen and R. Dessy, "Surface  
Acoustic Wave Probes for Chemical Analysis", Analytical Chemistry,  
Vol. 51, No. 9, August 1979, pp. 1458-1464), considerable interest in  
the use of surface acoustic wave (SAW) devices for chemical sensing has  
developed, and a review thereon has been published. D. S. Ballantine, Jr.  
30 and H. Wohltjen, "Surface Acoustic Waves", Analytical Chemistry,

Vol. 61, No. 11, June 1989, pp. 704A-715A.

SAW pressure measuring devices of the prior art are based on the change in resonant frequency caused by the mechanical force of pressure on the piezoelectric material of the SAW device. If the piezoelectric material is fabricated as a thin membrane and arranged in such a way that the force of pressure causes the membrane to distort or flex, the sensitivity of the device can be enhanced somewhat. U.S. patent 4,100,811. However, SAW pressure sensors of this type lack sensitivity for the measurement of pressures below 100 Pa.

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#### Summary of the Invention

It is accordingly a primary object of the present invention to overcome difficulties presented by prior art devices and provide a transducer which is useful in measuring absolute gas-state oxygen pressure from low pressures (pressures less than 100 Pa) to atmospheric pressure ( $1.01 \times 10^5$  Pa).

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It is also a primary object of the present invention to provide a highly sensitive air pressure sensor.

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These and other objects and their attending benefits are achieved by providing a surface acoustic wave (SAW) device, the piezoelectric material of which is coated with a chemical that will selectively and reversibly bind oxygen. Since air is 20.9% oxygen, this device will serve as an air pressure sensor with high sensitivity.

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#### Brief Description of the Drawings

For a more complete understanding of the present invention, including its objects and attending benefits, reference should be made to the Description of the Preferred Embodiments, which is set forth in detail

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below. This Description should be read together with the accompanying drawings, wherein:

FIG. 1 is a schematic diagram of a surface acoustic wave (SAW) oxygen pressure sensor according to the present invention;

5 FIG. 2 is a structural formula showing the oxygen binding  $\text{Co(II)C}_{1/2}$  picnic-basket porphyrin with poly(octylmethacrylate-co-vinylpyridine) providing the axial ligand;

FIG. 3 is a typical frequency oxygen pressure response curve for an SAW oxygen pressure sensor according to the present invention; and

10 FIG. 4 is the actual frequency/oxygen pressure response curve for the SAW oxygen pressure sensor described in the Example, *infra*.

#### Description of the Preferred Embodiments

15 This invention relates to a new transducer for the measurement of absolute gas-state oxygen pressure from low pressures (less than 100 Pa) to atmospheric pressure ( $1.01 \times 10^5$  Pa), and is based on a surface acoustic wave (SAW) device with a coating that will selectively and reversibly bind oxygen. This invention may also be used as a sensitive  
20 gaseous oxygen detector.

The piezoelectric material of an SAW device (see, e.g., U.S. 4,100,811) is coated with a chemical which will selectively and reversibly bind oxygen. When oxygen is bound by the coating on the SAW device the mass of the coating increases by an amount equal to the mass of the  
25 bound oxygen. The resonant frequency of the SAW device is given by the equation:

$$\Delta f = (k_1 + k_2) f^2 \left( \frac{m}{A} \right)$$

where

- $\Delta f$  = SAW resonance frequency change (Hz)
- $k_1$  =  $-9.33 \times 10^{-8} \text{ m}^2\text{s/kg}$ ,  $k_2 = -4.16 \times 10^{-8} \text{ m}^2\text{s/kg}$  for YX quartz oscillator
- 5  $f$  = SAW device resonance frequency (Hz)
- $m$  = mass of the coating (kg)
- $A$  = coated area ( $\text{m}^2$ ).

An increase in the mass of the coating caused by the bound oxygen  
10 causes a corresponding decrease in the resonant frequency of the SAW device. A diagram of the device is shown in FIG. 1. The fundamental resonant frequency of the uncoated SAW device is determined by the piezoelectric material and fabrication of the electrodes, but greater sensitivity is achievable if it has a resonant frequency greater than 100  
15 megahertz (MHz). The upper frequency is limited by electrode fabrication constraints. Devices having resonant frequencies of 158 MHz or 200 MHz were used for the embodiment given herein.

The coating may be prepared from, but is not limited to, any one of numerous oxygen binding compounds, including the oxygen-binding  
20 porphyrins, Salen Schiff-bases, and lacunar cyclidines. The requirements of the oxygen-binding compound in the coating on the SAW device are:

The coating should have the appropriate equilibrium constant (binding constant) for the reaction: Binding Agent +  $\text{O}_2 = \text{Binding Agent} \cdot \text{O}_2$ .

25 Oxygen-binding must be rapid and reversible.

The coating must be stable and not undergo oxidation.

The compound must be amenable to coating or bonding onto the surface of the SAW device.

It is convenient to define the binding constant as the partial  
30 pressure of oxygen when one-half the available oxygen sites in the

coating are filled with oxygen. The following designations are used:

$P_{O_2}$  = partial pressure of oxygen (torr)

$P_{1/2O_2}$  = the partial pressure of oxygen when one-half of the binding sites are occupied.

- 5 The relationship between  $P_{1/2O_2}$  and the standard equilibrium constant of  $P_{1/2O_2} = 1/K_{eq}$ .

The preferred embodiment of the invention uses coatings containing the oxygen-binding porphyrins. The picket-fence porphyrins and the picnic-basket porphyrins (PBP) (as understood by those of skill in  
10 the art) are preferred because they are stable, bind oxygen reversibly, and may be synthetically modified to control the binding constant. The formula and structure of a typical picnic-basket porphyrin is shown in FIG. 2. In addition to the possibility of changing the central metal ion (Co in FIG. 2), the length of the bridge or "handle" can be changed to change  
15 the oxygen binding constant. The bridging group of the PBP used for this invention consists of a  $-OCH_2-$  unit between the isophthalate rings which are joined to the porphyrin ring by the amide linkages. This PBP is designated as  $C_{1/2}$ PBP. The ability to modify the binding constant of the active ingredient of the coating is important because the binding constant  
20 determines the optimum pressure-measurement range for the invention.

The central metal ion such as Co(II) or Fe(II) of an oxygen-binding porphyrin has six bond sites. Four are occupied by nitrogens from the porphyrin molecule. The fifth must be occupied by an electron pair donor molecule called the axial ligand, and the sixth site can bind oxygen  
25 reversibly. SAW device coatings based on oxygen-binding porphyrins must contain a substance that will serve as the axial ligand. This substance may be but is not limited to, pyridine, methyl imidazole, 1,5-dicycloimidazole or a substance which will furnish these types of chemical groups. An example of a substance which will furnish an axial  
30 ligand to the oxygen-binding porphyrin is a copolymer containing an axial

ligand along the polymer chain, such as poly(octylmethacrylate-co-vinylpyridine).

A typical frequency/oxygen-pressure response curve is illustrated by FIG. 3. The optimum pressure-measurement range for the coating depicted in FIG. 3 is between 1.0 kPa and 100 kPa. For a given pressure range there is an optimum binding constant for the activity ingredient of the coating. Table I gives the optimum values of  $P_{1/2}$  for different oxygen (and air) pressure ranges. The minimum pressure of each range is based on the pressure required to produce a signal change of 500 Hz and the maximum pressure for each range is that required to saturate 70% of the binding sites. Since air has a constant concentration of oxygen this invention may be used to measure air pressure.

TABLE I		
OPTIMUM BINDING CONSTANTS FOR SAW DEVICE COATINGS		
Oxygen Pressure Range (kPa)	Air Pressure Range(kPa)	Binding Constant, $P_{1/2}$ (kPa)
0.002 - 0.3	0.013 - 1.3	0.11
0.010 - 1.3	0.070 - 6.7	0.57
0.130 - 13.0	0.070 - 67.0	5.70
0.700 - 53.0	3.300 - 267.0	29.00
1.300 - 133.0	6.700 - 667.0	57.00
2.700 - 267.0	13.000 - 1333.0	115.00

#### Example

A 158 MHz SAW device (Microsensor Systems, Incorporated, 62 Corporate Court, Bowling Green, Kentucky 42103) was spray-coated in a nitrogen atmosphere. The coating solution was 99.24% toluene, 0.35% 1,5-dicyclohexylimidazole, and 0.41% cobalt(II) $C_{1/2}$  picket-fence porphyrin. The SAW device was then cured at 60°C under nitrogen for



30 minutes. The frequency response to oxygen (or Air) pressure was measured with a CEM-158-B dual delay line oscillator system (Microsensor Systems, Incorporated). The device was suitable for measuring oxygen pressure in the range of 0.25 KPa-26 KPa with a  
5 sensitivity ranging from 436 HZ/kPa to 6 Hz/kPa. The response of the device is illustrated by FIG. 4.

What is claimed is:

## SURFACE ACOUSTIC WAVE OXYGEN PRESSURE SENSOR

Abstract of the Disclosure

5           A transducer for the measurement of absolute gas-state oxygen pressure from pressures of less than 100 Pa to atmospheric pressure ( $1.01 \times 10^5$  Pa) is based on a standard surface acoustic wave (SAW) device. The piezoelectric material of the SAW device is coated with a compound which will selectively and reversibly bind oxygen. When  
10 oxygen is bound by the coating, the mass of the coating increases by an amount equal to the mass of the bound oxygen. Such an increase in the mass of the coating causes a corresponding decrease in the resonant frequency of the SAW device.

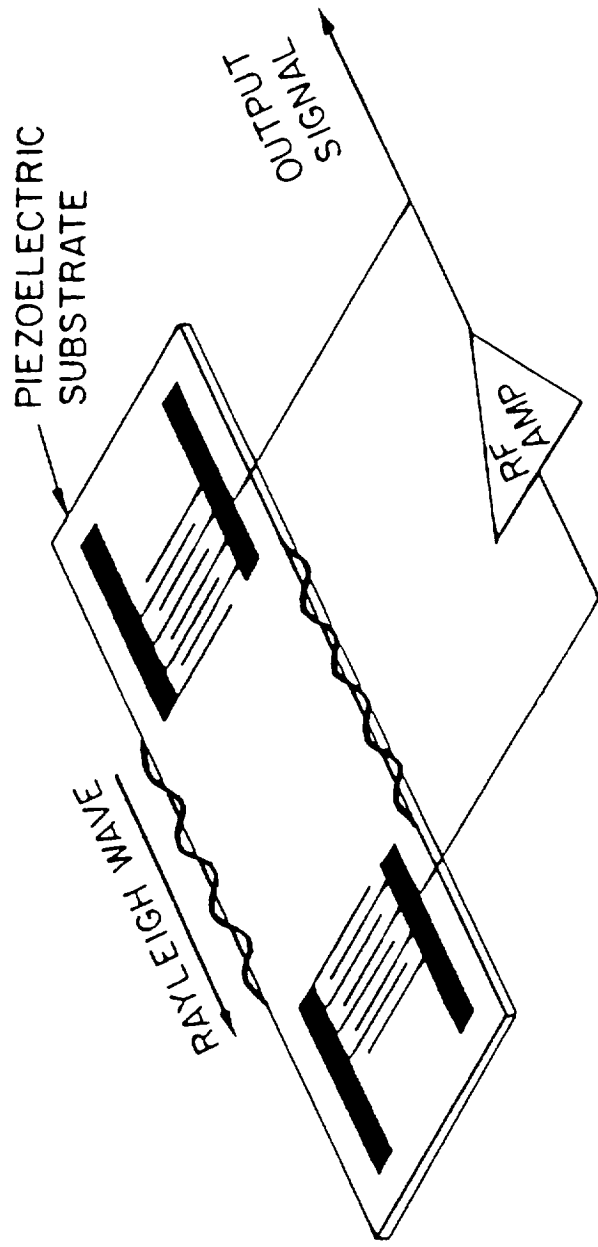


FIG. 1

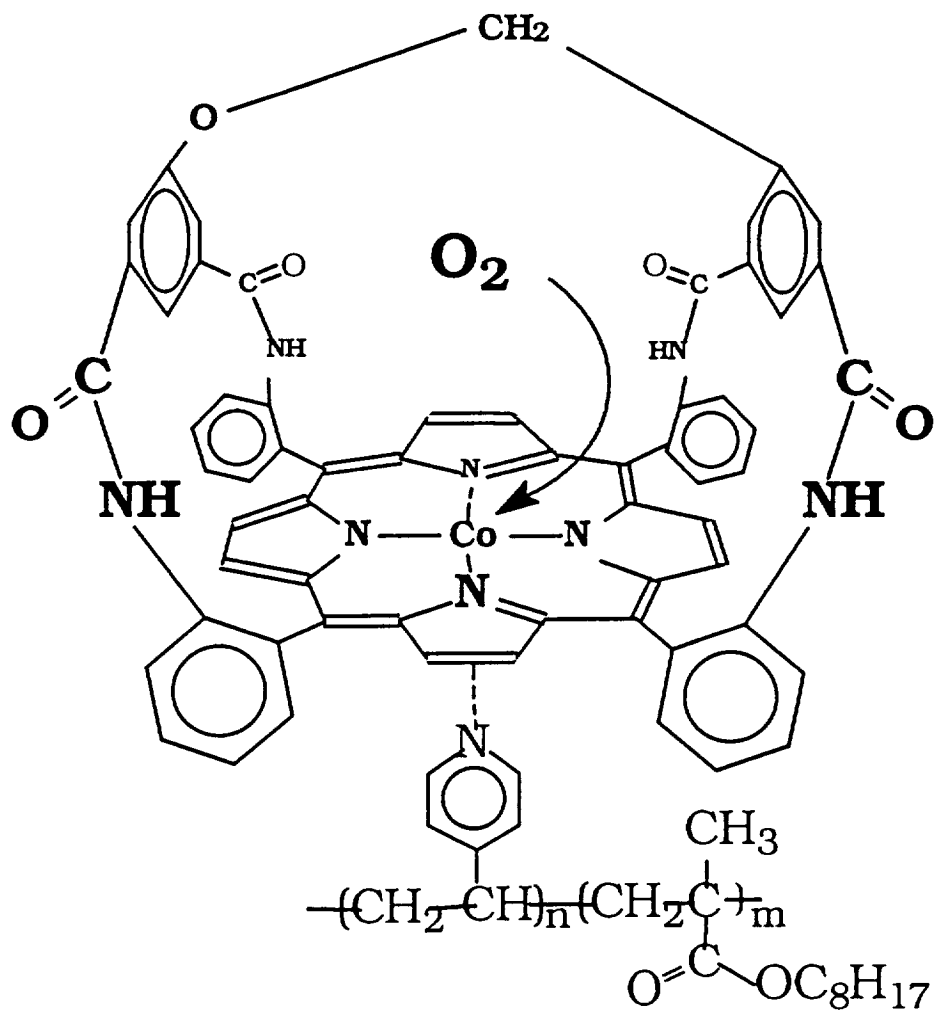


FIG. 2

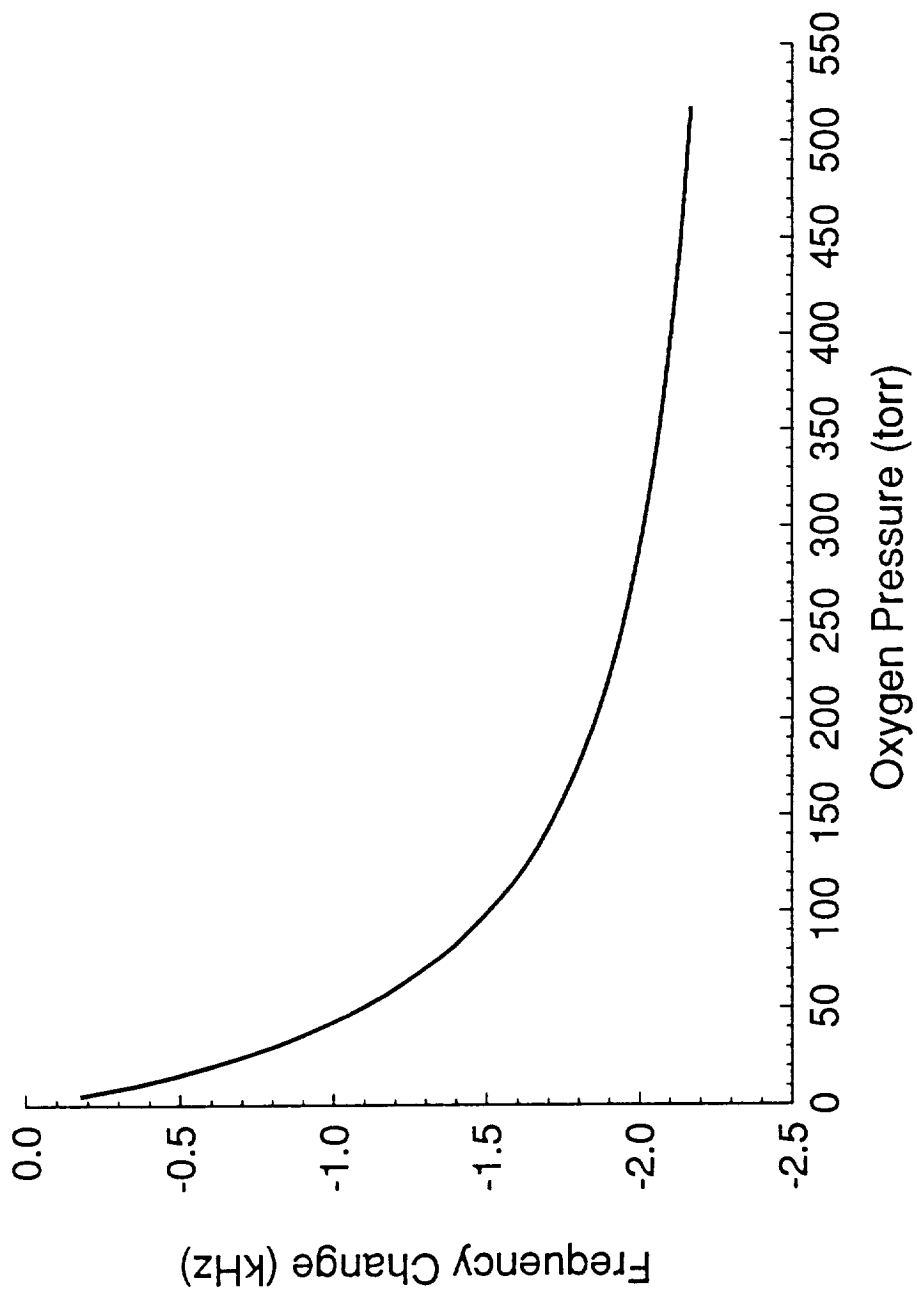


FIG. 3

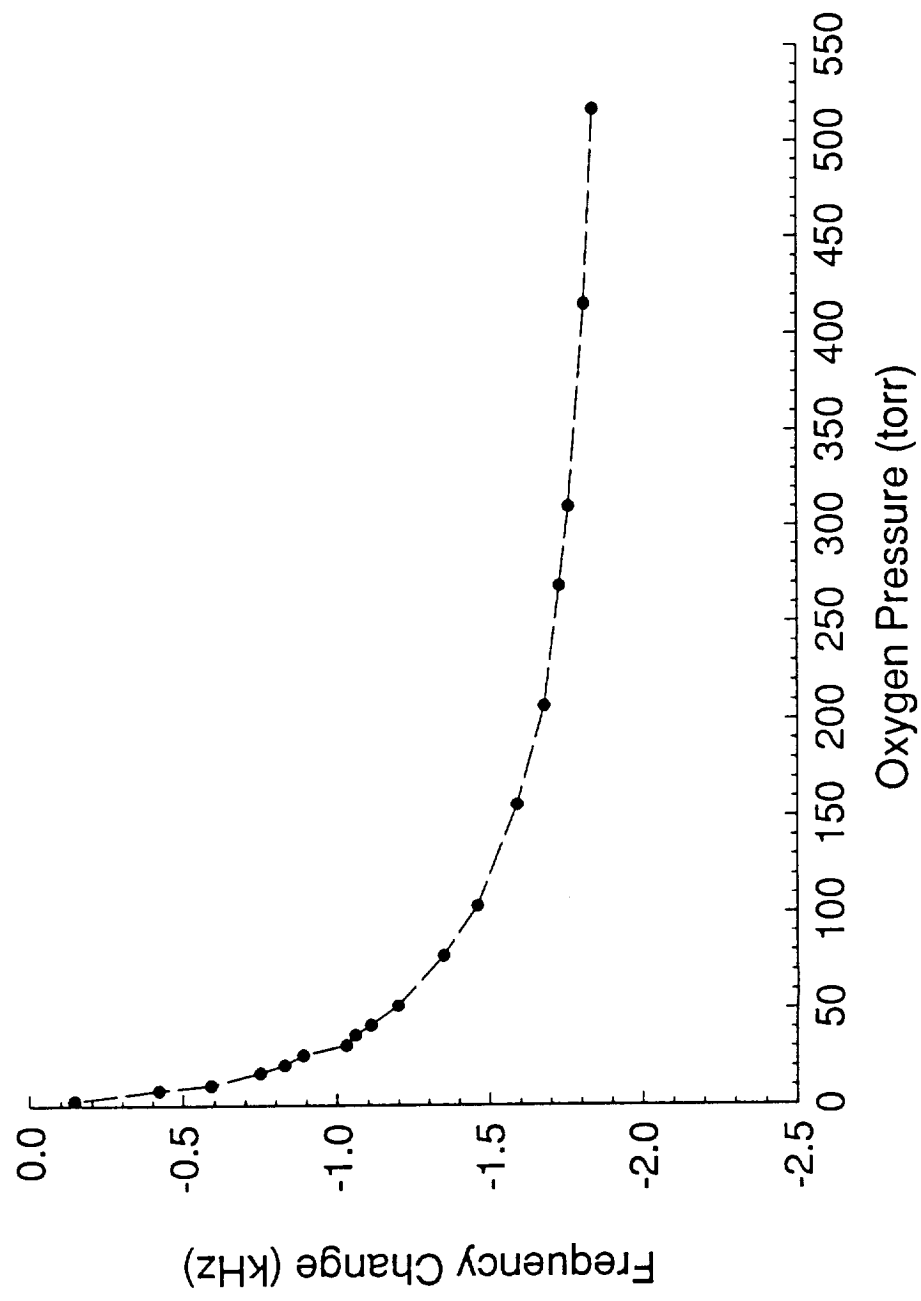


FIG. 4